Hydrogen cycling behavior of Reactive Hydride Composites of NaF-NaH-MgB_2 investigated by in-situ powder diffraction

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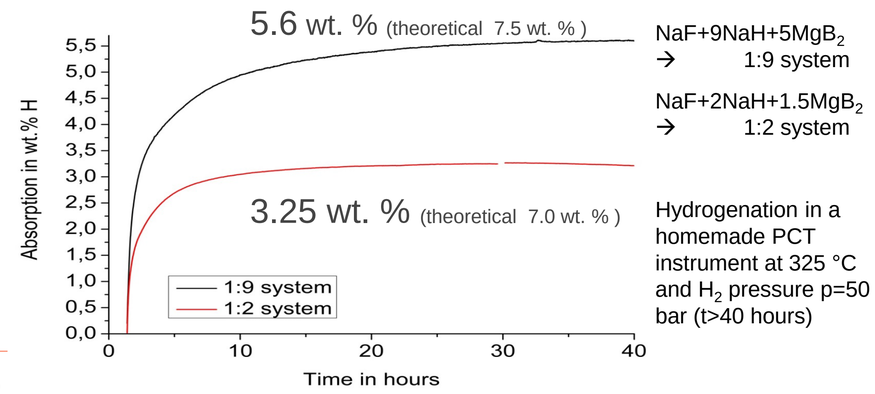
Abstract

The hydrogenation and dehydrogenation properties of Reactive Hydride Composites (RHC) NaF+9NaH+5MgB_2 (1:9 system) and NaF+2NaH+1.5MgB_2 (1:2 system) with theoretical hydrogen absorption capacities of 7.5 wt.% and 7.0 wt.%, respectively, are studied. A high capacity of 6 wt.% H is measured in the first cycle, but it decreases to almost 3 wt.% H after 5 cycles for NaF+9NaH+5MgB_2. In-situ Synchrotron Radiation Powder X-ray Diffraction has been used to follow the hydrogen absorption, desorption and re-absorption reactions. The first absorption proceeded rather slowly and took hours to complete at 325°C under 50 bar H_2. However, after desorption at 510°C, rehydrogenation proceeded in the matter of minutes at the same temperature. $NaBH_4$ is the main phase in the hydrogenated state for both systems.

Hydrogenation



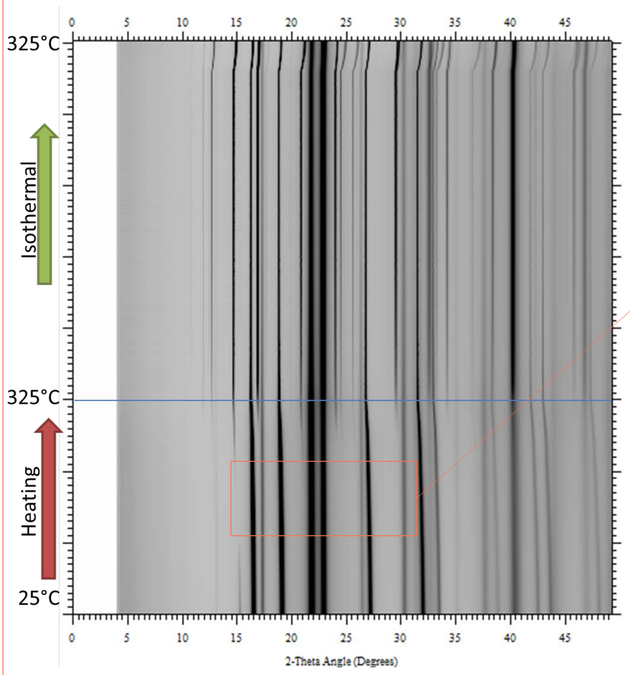
NaF+9NaH+5MgB_2 → 1:9 system

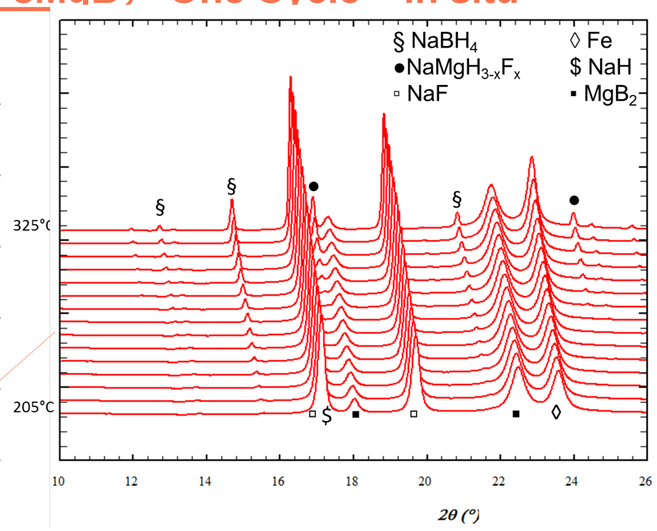
NaF+2NaH+1.5MgB_2 → 1:2 system

Hydrogenation in a homemade PCT instrument at 325 °C and H_2 pressure p=50 bar (t>40 hours)

NaF+9NaH+5MgB_2 - One Cycle – in situ

Hydrogenation (50 bar)



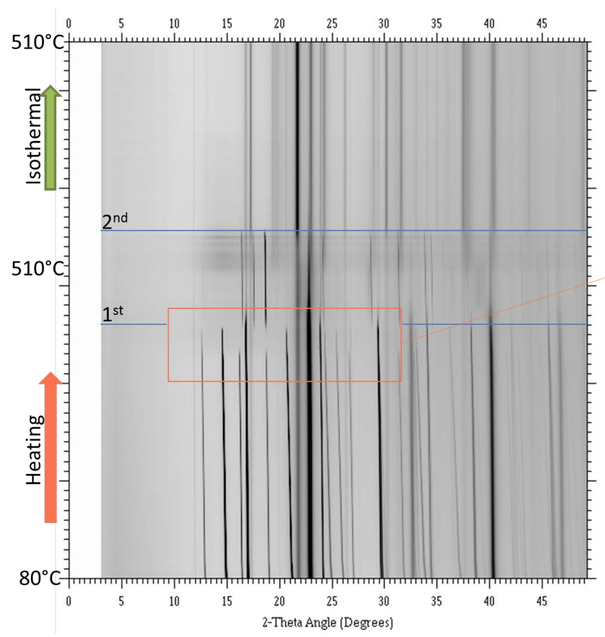


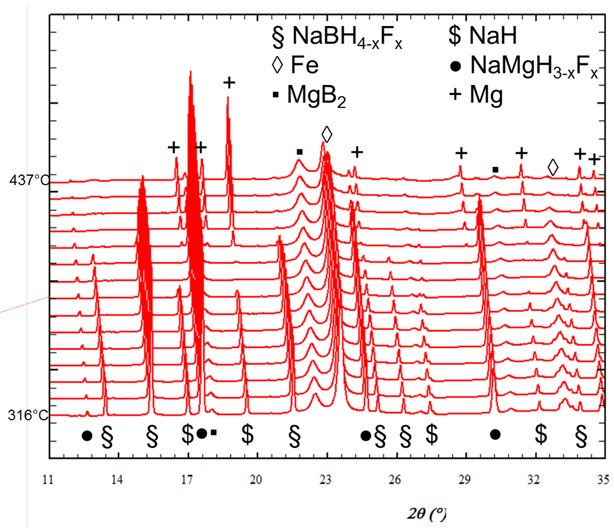
Formation of $NaBH_4$ (220°C)

$NaMgH_{3-x}F_x$ (280°C)

$xNaF_{(s)} + (1.5-x)NaH_{(s)} + MgB_{2(s)} + 1.75H_{2(g)} \rightarrow 0.5NaBH_{4(s)} + NaMgH_{3-x}F_{x(s)}$

Dehydrogenation (1 bar)

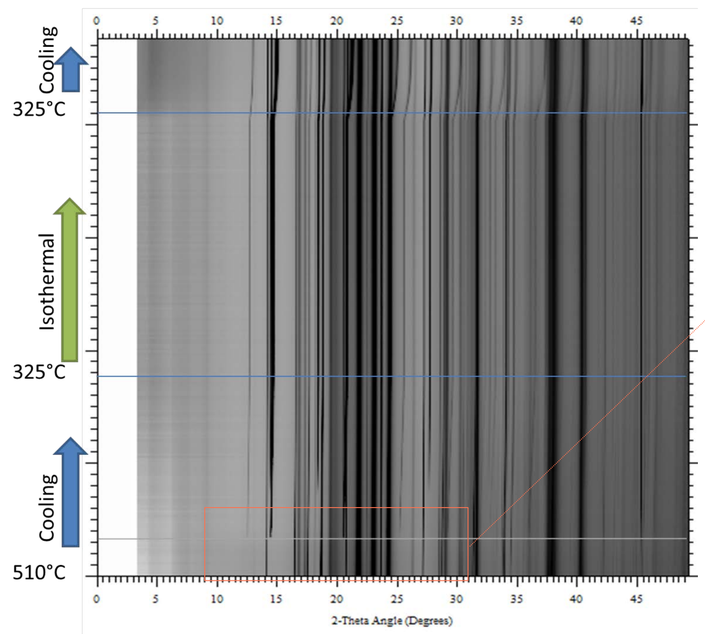


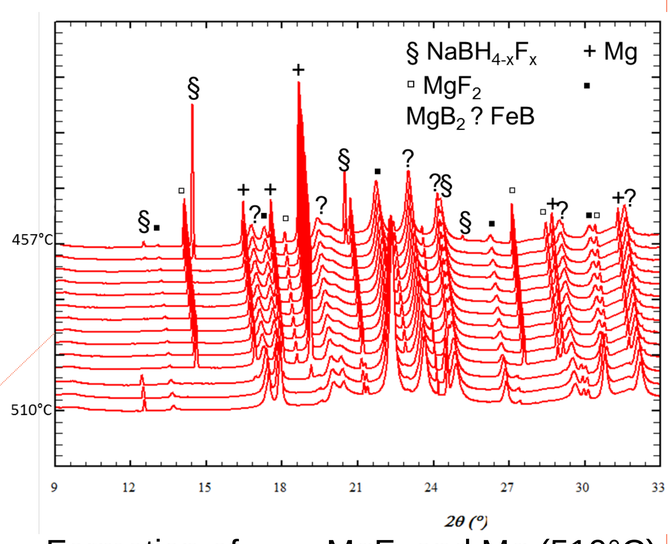


1st : $NaH_{(s)} + NaMgH_{3-x}F_{x(s)} + NaBH_{4(s)} \rightarrow Mg_{(s)} + NaBH_{4-x}F_{x(l)} + 2Na_{(l)} + 2H_{2(g)}$

2nd : $Mg_{(s)} + 2NaBH_{4(l)} \rightarrow MgB_{2(s)} + 2Na_{(l)} + 4H_{2(g)}$

Re-Hydrogenation (50 bar)





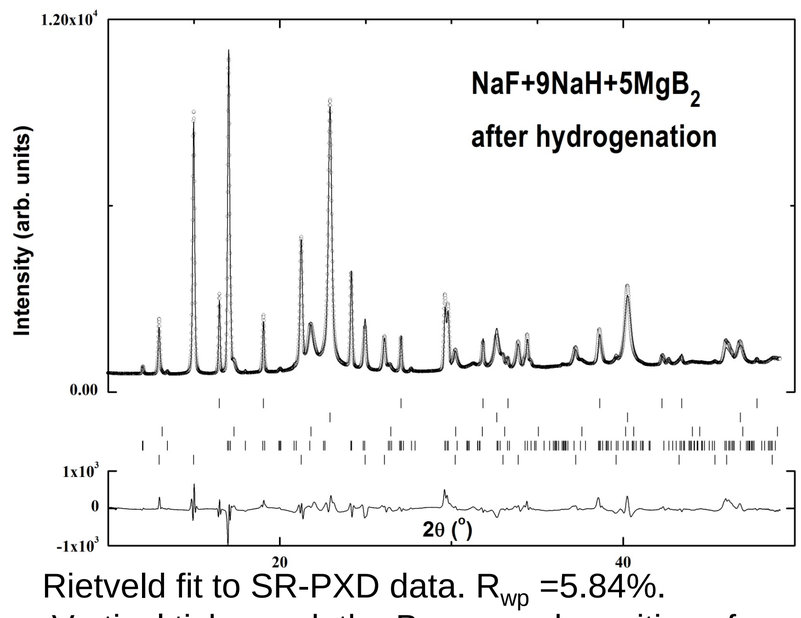
Formation of MgF_2 and Mg (510°C)

$NaBH_{4-y}F_y$ (460°C)

MgH_2 (430°C)

$MgB_{2(s)} + 2NaMgH_{3-x}F_{x(s)} + 3.5H_{2(g)} \rightarrow 0.5Mg_{(s)} + (x-y)MgF_{2(s)} + 2NaBH_{4-y}F_{y(s)} + (2.5-x+y)MgH_{2(s)}$

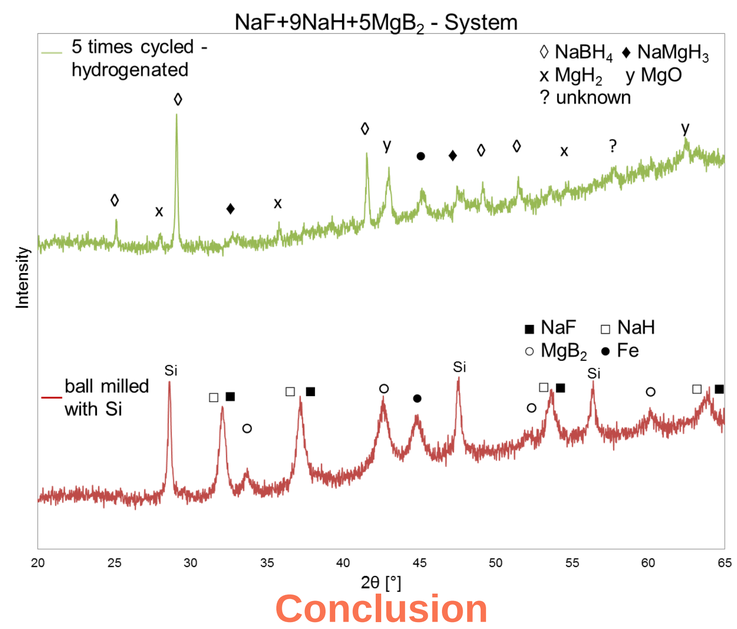
Rietveld Refinement after hydrogenation



Rietveld fit to SR-PXD data. R_{wp} =5.84%.
Vertical ticks mark the Bragg peak positions for

1. NaH	6.2 wt.%	2. Fe	9.74 wt.%
3. MgB_2	10.8wt.%	4. $NaMgH_3$	30.72 wt.%
5. $NaBH_4$	42.47 wt.%		

Cycling



Conclusion

- Presence of fluorine allows hydrogenation at milder conditions: formation of $NaBH_4$ at 220 °C compared to 380 °C for F-free composite [1, 2]
- 50% better hydrogen uptake and reversibility of the 1:9 system of approx. 58% after 5 cycles compared to F-free composite [1]
- Observation of FeB as well as MgF_2 and elemental Mg after rehydrogenation at 510°C, not at 325°C, which indicates a more suitable reaction path way at 325 °C

Outlook

Question:
Could selective hydrogenation in temperature range of 220°C to 250 °C avoid the formation of undesired $NaMgH_{3-x}F_x$?

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References

[1] Nwakwuo, C.C., et al., *Microstructural analysis of hydrogen absorption in 2NaH+MgB(2).* Scripta Materialia, 2011. 64(4): p. 351-354.

[2] Pistidda, C., et al., *Pressure Effect on the 2NaH+MgB(2) Hydrogen Absorption Reaction.* Journal of Physical Chemistry C, 2010. 114(49): p. 21816-21823.